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NEW LOW TEMPERATURE, HIGH ENERGY DENSITY BATTERY SYSTEMS.(U)

JUL 78 J K ERBACHER, C L HUSSEY, J C NARDI

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FRANK J. SEILER RESEARCH LABORATORY

FJSRL TECHNICAL REPORT -78-0007

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NEW LOW TEMPERATURE, HIGH ENERGY DENSITY  
BATTERY SYSTEMS

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PROJECT 2303

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AIR FORCE SYSTEMS COMMAND

UNITED STATES AIR FORCE

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This document was prepared by the Electrochemistry Division, Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory, United States Air Force Academy, Colorado. The research was conducted under Project Work Unit Number 2303-F2-07, "Pelletized Thermal Batteries." Major John K. Erbacher was the Project Scientist in charge of the work.

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This report has been reviewed by the Chief Scientist and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The thermal battery work unit of the Frank J. Seiler Research Laboratory (AFSC), USAF Academy, CO, has conceived, designed, and constructed laboratory prototype thermal battery single cells which utilize the inherent high energy of reaction of aluminum and aluminum alloys with transition metal chlorides. The individual cells are comprised of an aluminum or lithium-aluminum alloy anode and an immobilized liquid sodium tetrachloroaluminate electrolyte. The electrolyte is completely immobilized by the addition of finely divided silica. The cell cathode is either molybdenum pentachloride or cupric chloride		

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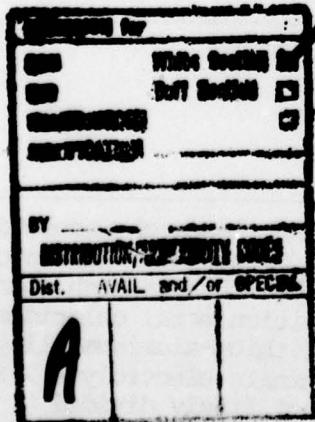
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in intimate contact with a graphite current collector. Trilayer pellets were constructed incorporating the anode, electrolyte and cathode.

The discharge behavior was studied from 175-275°C at current densities from 2-120 millamps per square centimeter to evaluate the operational temperature ranges and current density characteristics of the two systems.



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The recent development and interest in lightweight communication and arming systems, especially for airborne applications has provided an impetus for basic research on new electrochemical power sources. These new power sources must be capable of high energy output, unlimited storage life, rapid and reliable activation and be able to withstand high spin rates, severe shock, and vibrational environments. To meet these operational and performance requirements previous batteries utilized molten salt electrolytes operating in the 400-525°C temperature range which were inactive until heated above the melting point of the electrolyte. These thermally activated batteries (thermal batteries) required quantities of insulating material to maintain their operational temperatures and to insulate surrounding electronic components from the heat generated during activation and operation. They also utilize chromium(VI) compounds that are known health hazards and one of the pyrotechnic components, zirconium, has been in short supply because of particle size manufacturing process difficulties.

Laboratory prototype thermal battery single cells were conceived, designed, and constructed in this laboratory which utilize the inherent high energy of reaction of aluminum and aluminum alloys with transition metal chlorides in a low temperature molten salt electrolyte. These low temperature thermal cells were evaluated using single cell testing techniques previously described (1). The particular electrochemical system under investigation utilizes a LiAl alloy anode, a NaCl-saturated  $\text{AlCl}_3$  electrolyte, m.p. 158°C, and a  $\text{MoCl}_5$  or  $\text{CuCl}_2$  cathode operating at temperatures between 175°C and 250°C. This electrochemical system is a candidate to replace or complement current thermal battery systems operating at much higher temperatures (2). Previous work (2,3) in this laboratory had identified molybdenum(V) chloride and copper(II) chloride as potentially excellent cathodes utilizing this electrolyte. The purpose of the work was to study these two cathodes with respect to variables associated with current production thermal batteries, such as (1) graphite content, (2) alloy anode composition, (3) particle size, (4) anode/cathode electrolyte ratios, (5) current density, and (6) temperature.

Trilayer single cells (Figure 1) containing the anode, separator, and cathode were fabricated in a Carver die. Pressures used to compact the successively added layers were 16,700, 23,000 and 29,200 lb/in<sup>2</sup> for anode, separator and cathode layers respectively. The cathode layer contained graphite as the current collector. Typical single cell compositions for both the  $\text{MoCl}_5$  and  $\text{CuCl}_2$  cathodes are given in Table I. Differences in the composition of the single cells for the two cathodes are the result of two different approaches to the study of single cell performance.

For the  $\text{MoCl}_5$  cathode the aim was to arrive at an optimized composition that would yield the highest energy density possible from the cell. Fisher graphite was used because it was the graphite selected in the development of the  $\text{LiAl}/\text{MoCl}_5$  thermal battery by the Eureka Advanced Science Corporation (4). Use of the same graphite allowed direct comparison with their data. For the  $\text{CuCl}_2$  cathode our goal was to assess the effect of different commercially available active anode and cathode materials on single cell performance.

The study of the  $\text{MoCl}_5$  cathode (3) showed that the optimum energy density was obtained using the 60.2 a/o  $\text{LiAl}$  alloy, a 30-50 mesh  $\text{MoCl}_5$  particle size, 0.230 g graphite in the cathode, and the anode/cathode/electrolyte ratios depicted in Table IA. The optimal single cell configuration delivered 38 W-hr/lb to zero volts at a discharge rate of 15 mA/cm<sup>2</sup> at 175°C.

Table I. Typical Compositions

A. For the  $\text{LiAl}/\text{MoCl}_5$  Single Cell

Section	Wt (g)	Component
Anode	0.270	60.2 a/o $\text{LiAl}$
Separator	0.780	EB Mixture <sup>a</sup>
Cathode	0.640	EB Mixture <sup>a</sup>
	0.720	$\text{MoCl}_5$ (30-50 mesh)
	0.230	Graphite (Fisher)

B. For the  $\text{LiAl}/\text{CuCl}_2$  Single Cell

Anode	0.500	60.2 a/o $\text{LiAl}$
	0.500	EB Mixture <sup>a</sup>
Separator	0.900	EB Mixture <sup>a</sup>
Cathode	0.450	EB Mixture <sup>a</sup>
	0.500	$\text{CuCl}_2$ (50-100 mesh)
	0.160	Graphite (purified Superior)

<sup>a</sup>EB Mixture: Electrolyte (49.85 m/o  $\text{AlCl}_3$ -50.15 m/o  $\text{NaCl}$ ) + Binder (10 w/o Cab-o-Sil)

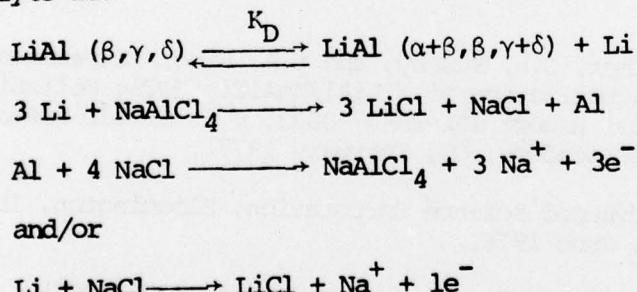
A new method for the analysis of discharge data (5) was applied to thermal battery single cell test data. This procedure requires a plot of the derivative discharge function,  $dQ/dV^*$ , versus the average voltage,  $\bar{V}^*$ . Such plots show  $\text{MoCl}_5$  single cells, using Fisher graphite at operating temperatures of 175-275°C. As many as six separate discharge peaks with the major portion of the discharge reaction

\* $dQ$  is the change in coulombs,  $dV$  is the change in potential, and  $\bar{V}$  is the average potential of the  $dQ/dV$  increment.

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shifted to the lower potentials with increasing temperatures. Previous studies by Phillips and Osteryoung (6) had indicated that there were only three discharge steps at 175°C for MoCl<sub>5</sub>. To reconcile the test data additional experiments utilizing a purified Superior graphite (7) were accomplished. This new data confirmed that there were only three peaks in the discharge curve for MoCl<sub>5</sub> and that the additional peaks were due to trace iron impurities in the Fisher graphite. Supporting this conclusion X-ray analysis unequivocally established iron contamination. The purified graphite samples also confirmed the fall-off in cell performance due to increasing operation temperature. Apparently the decreased performance at higher temperatures is due to the low melting and boiling points of the MoCl<sub>5</sub>, 195°C and 268°C, respectively (8). This may limit the application of the MoCl<sub>5</sub> thermal battery to the temperature region between 175°C and 250°C (9).

The second phase was a detailed study on the effect of lithium-aluminum alloy anode composition using a CuCl<sub>2</sub> cathode as depicted in Table IB. The results indicate that the optimum anode was 60.2 a/o LiAl. Data for a 48.0 a/o alloy was significant in light of: (a) the voltage spike phenomena observed during temperature activation; (b) an observed identical open circuit voltage for LiAl alloys versus pure Al anodes; (c) the reported behavior of LiAl alloy anodes in other electrolytes; and (d), the phase diagram reported by Hansen (12) and Myles (13). This data suggests that Li is produced by dissociation of the alloy which reacts with the electrolyte to produce Al. The Al is then subsequently oxidized during cell discharge. Variations in performance of anode alloys results from different dissociation constants (K<sub>D</sub>) for various LiAl alloys. A probable discharge mechanism for LiAl alloys in an NaCl-AlCl<sub>3</sub> electrolyte is:



Confirmation of this proposed mechanism will depend on analysis of single cell electrolytes after discharge and determination of the phase diagram for the LiCl-NaCl-AlCl<sub>3</sub> ternary electrolyte.

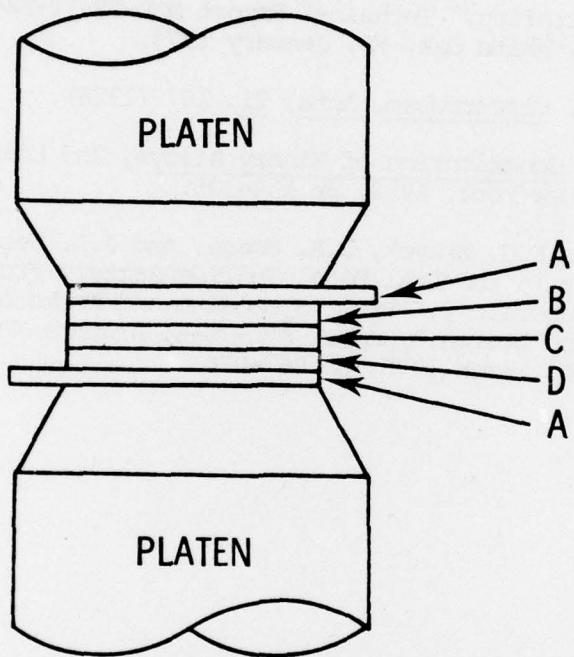
The success of the basic research program on low temperature thermal battery systems at the FJSRL has been demonstrated by the transition of the work reported here into exploratory development by the Air Force Aeropropulsion Laboratory (AFAPL). The initial feasibility study on the new system conducted under an AFAPL contract indicated that it is capable of meeting the performance requirements for existing thermal batteries as well as operating at much lower temperatures. Benefits from the low temperature operation will include reduced weight, volume, insulation, and conservation of critical pyrotechnic component supplies. Additional safety benefits will also be realized in that manufacturing health hazards associated with carcinogenic chromium(VI) compounds are avoided.

The basic research program on low temperature thermal battery systems at the FJSRL has resulted in the first new electrochemical system for thermal battery applications in 25 years.

#### REFERENCES

1. C.L. Hussey, J.K. Erbacher, and L.A. King, "High Energy Density Pelletized Aluminum Chloride Thermal Batteries," Technical Report SRL-TR-76-0003, F.J. Seiler Research Laboratory (AFSC), USAF Academy, CO, January 1976.
2. J.K. Erbacher, C.L. Hussey, and L.A. King, "The Discharge Behavior of a  $\text{LiAl}/\text{NaAlCl}_4/\text{CuCl}_2$  Pelletized Thermal Cell," Technical Report SRL-TR-77-0001, F.J. Seiler Research Laboratory (AFSC), USAF Academy, CO, February 1977.
3. J.C. Nardi, J.K. Erbacher, C.L. Hussey, and L.A. King, "Experimental Optimization and Characterization of a  $\text{LiAl}/\text{NaAlCl}_4/\text{MoCl}_5$  Pelletized Thermal Cell," Technical Report SRL-TR-77-0002, F.J. Seiler Research Laboratory (AFSC), USAF Academy, CO, February 1977.
4. D. Ryan, The Eureka Advanced Science Corporation, Bloomington, IL, private communication, June 1976.
5. L. Balewski and J.P. Brenet, Electrochem. Tech., 5, 527 (1967).
6. J. Phillips and R.A. Osteryoung, Colorado State University, Fort Collins, CO, unpublished manuscript, 1976.
7. G.D. Brabson, J.K. Erbacher, L.A. King, and D.W. Seegmiller, "Exploratory Aluminum Chlorine Thermally Activated Battery: Single Cell Experiments," Technical Report SRL-TR-76-0002, F.J. Seiler Research Laboratory (AFSC), USAF Academy, CO, January 1976.

8. J.A. Dean, Ed., Lange's Handbook of Chemistry, 11th Edition, McGraw-Hill Book Co., New York, 1973, p 4-81.
9. D.M. Ryan and L.C. Bricker, "High Energy Density Pelletized Aluminum Chlorine Thermal Batteries," Technical Report AFATL-TR-77-12, Air Force Aeropropulsion Laboratory, Wright-Patterson AFB, OH, April 1977.
10. S.D. James, "Preliminary Study of a Lithium Aluminum Electrode for Thermal Batteries," Technical Report NOL-TR-72-224, Naval Ordnance Laboratory, White Oak, MD, January 1973.
11. S.D. James, Electrochem. Acta, 21, 157 (1976).
12. M. Hansen, Constitution of Binary Alloys, 2nd Edition, McGraw-Hill Book Co., New York, 1958, pp 104-105.
13. K.M. Myles, F.C. Mrayek, J.A. Smaga, and J.L. Settle, "Materials Development in the LiAl/Metal Sulfide Battery Program at Argonne National Laboratory," Proc. Symposium and Workshop of Adv. Battery Research and Design," Report ANL-76-8, Argonne National Laboratory, Chicago, IL, March 1976, pp B67-B70.



A - current collectors

B - anode

C - electrolyte

D - catholyte

Figure 1. Typical Cell Configuration Between Heated Platens